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| Title: POTENTIOMETRIC $NO_x$ SENSORS BASED ON YTTRIA-STABILIZED ZIRCONIA WITH ZEOLITE MODIFIED ELECTRODE | | |

## VERIFIED STATEMENT (DECLARATION) UNDER 37 C.F.R. §1.131

I, Prabir K. Dutta, hereby declare that I am over 21 years of age, of sound mind, capable of making this declaration, and fully competent to testify concerning the matters stated herein. I have personal knowledge of each of the matters stated herein.

I am one of the inventors of the above-referenced patent application. I understand that the United States Patent and Trademark Office has rejected all claims presently pending in the above-referenced application on the basis of "Microporous zeolite modified yttria stabilized zirconia (YSZ) sensors for nitric oxide (NO) determination in harsh environments" by Szabo et al. (hereinafter "the Szabo article") published as an uncorrected proof by Sensors and Actuators B Chemical sometime after October 31, 2001, a copy of which is attached hereto as Exhibit 1.

The above referenced patent application names Nicholas F. Szabo, Hongbin Du, Sheikh A. Akbar, and Prabir K. Dutta as the inventors. The authors of the Szabo article are Nicholas F. Szabo, Hongbin Du, Sheikh A. Akbar, Prabir K. Dutta, and Ahmed Soliman.

The Szabo article discloses the inventive efforts of Nicholas F. Szabo, Hongbin Du, Sheikh A. Akbar, and Prabir K. Dutta.

Ahmed Soliman worked under the direction and control of the inventors of the above-identified patent application by testing the performance of the inventive $NO_x$ sensor and assisted in the preparation of the Szabo article. Thus, Ahmed Soliman is properly named as an author; however, Mr. Soliman did not contribute to either the conception or reduction to practice of the invention claimed in the above-referenced patent application. Accordingly, Mr. Soliman acted under the direction and control of the inventors, without contributing to the invention.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 10001 of Title 18 of the United States Code, and that such willful false statements made jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

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# Microporous zeolite modified yttria stabilized zirconia (YSZ) sensors for nitric oxide (NO) determination in harsh environments

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**Abstract**

This study is focused on development of a nitrogen monoxide (NO) sensor capable of operation in harsh environments, as exemplified by automotive exhaust streams. The basis of the sensor is a mixed potential response generated by exposure of gases to a platinum–yttria stabilized zirconia (Pt–YSZ) interface. The asymmetry between the two Pt electrodes on YSZ is generated by covering one of the electrodes with a zeolite, which helps promote the $NO/NO_2$ equilibrium prior to the gases reaching the electrochemically active interface. The mixed potential generated is logarithmically related to NO concentration (0–1000 ppm) at temperatures between 500 and 700 °C, the optimum temperature being 500 °C. The microporosity of the zeolite makes it permeable to oxygen, thus, minimizing the interference to $O_2$. The sensor shows interference from CO and $NO_2$. Three sensor designs have been examined, including a planar design that can be packaged appropriately for surviving automotive exhaust streams. Automotive tests indicate that the sensor is capable of detecting $NO_x$ in engine exhausts.
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*Keywords:* Zeolite Y; Yttria stabilized zirconia (YSZ) sensors; Infrared spectroscopy mixed potential, automotive exhaust sensor

## 1. Introduction

Processes that involve combustion of fossil fuels produce various emission gases such as nitrogen oxides ($NO_x$), carbon monoxide (CO), carbon dioxide ($CO_2$), hydrocarbons ($C_nH_{2n+2}$, referred to as HC), and sulfur oxides ($SO_x$) [1]. These combustion sources can include gas heating furnaces, power plants, and internal combustion engines. Other anthropogenic sources of these gases can arise from non-combustion sources, an example being formation of $NO_x$ in chemical plants during nitric acid production or chemical nitration with subsequent venting into the atmosphere via stacks [2]. $NO_x$ includes several nitrogen oxide species, $N_2O$, NO, $N_2O_3$ and $NO_2$, with nitrogen in different oxidation states and their impact on the environment and health has been well documented [3,4]. Tighter federal regulations for automotive and power plant emissions have been instituted. To control these gas emissions, monitoring is essential. Various instrumental methods, such as infrared (IR) spectroscopy, chemiluminescence detection, and gas chromatography have been used to measure $NO_x$ species, but often have the disadvantage of large size and cost [5–7]. The use of high-temperature solid state gas sensors to monitor emissions in combustion related processes show great promise due to small size, lower cost, and real-time measurement capabilities [8].

Of particular interest to this study is the class of sensors based on mixed potential measurements. [9,10]. If several electrochemical reactions occur simultaneously on an electrode, the rates of these individual reactions determines the overall electrode potential and is referred to as the mixed potential (or corrosion potential in the corrosion literature). Often, a mixed potential sensor is composed of a solid electrolyte that is an oxygen ion conductor such as yttria stabilized zirconia (YSZ), and reactions involve oxidation/reduction of the sensing gas. For mixed potential systems, the voltage does not obey a Nernstian response with concentration of $O_2$, indicating a kinetic-based origin of the mixed potential. Bruser et al. presented one of the earliest papers on $NO_x$ determination with asymmetric electrodes (Pt and perovskites) on YSZ [11]. Miura et al. have examined various strategies for $NO_x$ sensing using zirconia based mixed potential sensors. Their focus was to evaluate a series of metal oxide electrodes and found that several spinel-type oxides, including $CdCr_2O_4$ and $CdMn_2O_4$ exhibited high $NO_x$ sensitivity [12–14].

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A class of compounds called zeolites show promise for use in harsh environment gas sensors. Zeolites are crystalline, microporous, hydrated aluminosilicates of interlinked $SiO_4$ and $AlO_4$ tetrahedra, in an infinitely extended three-dimensional network [15]. Zeolites have been used as catalysts for many reactions and in particular for the removal of noxious constituents present in automobile exhaust [16]. There have also been several accounts of utilizing zeolite materials for gas sensing at high-temperatures. For example, CO detection at 300 °C was accomplished using Au-$La_2O_3$/$SnO_2$ covered with a layer of the zeolite, ferrierite [17]. The addition of the zeolite served as a catalyst filter to allow selectivity for CO in the presence of $H_2$, $CH_4$, $C_2H_4$, $i$-$C_4H_{10}$ and $C_2H_5OH$. Zeolites deposited on a quartz crystal microbalance (QCM) have been utilized as sensors for gaseous molecules, e.g. Cu-ZSM-5 was used to detect NO in He at 348 K [18]. A similar study done at 423 K involving a thin layer of the zeolite faujasite on a QCM detected $SO_2$ in the presence of $O_2$ [19].

The purpose of this study was to develop a high-temperature NO sensor, without the need for an air reference, and with minimal interference by changing $O_2$ concentration and a simple design. We accomplished this objective by using YSZ packed or coated with a layer of microporous zeolite Y.

## 2. Experimental

### 2.1. Sensor designs

Three sensor designs based on the same principle were tested. The first (type I), displayed in Fig. 1, consisted of a YSZ pressed pellet with Pt electrodes mounted onto an alumina tube packed with zeolite NaY (LZY-52 from Union Carbide). The YSZ pellet was made from commercial YSZ powder (HSY-8, Zirconia Sales Inc., 8 mol% YSZ). The pellet was formed in a stainless steel die (Carver Inc.) under 10,000 psi on a Carver pellet press. The green pellet was put onto an alumina plate and sintered in a Lindberg Blue high-temperature box furnace at 1450 °C for 6 h with 6 °C/min heating and cooling rates. The final pellet dimensions were approximately 9 mm diameter and 2 mm thickness and had a white color. Pt ink (Englehard Corporation, lot #A4731) was painted on both sides of the pellet and Pt lead wires (Englehard Corporation, 31 AWG) were set into the wet Pt ink. The ink was then cured in a Lindberg Blue box furnace at 1250 °C for 2 h with a heating and cooling rate of 6 °C/min. The resulting electrodes had a metallic grey color. The pellet was then mounted onto an alumina tube (Coors Ceramics), approximately 1 inch in length, with a high-temperature inorganic adhesive, Ceramabond 569 (Aremco). Thus, one lead wire was on the outside of the tube and the other wire on the inside. The Ceramabond was then left to dry for 1–2 h at room temperature. The purpose of the tube is to hold zeolite powder, which was then packed on the inside as to cover the electrode. After final assembly the sensor was put into a tube furnace at 500 °C for a few hours to thermally stabilize before testing.

The second sensor design (type II) (Fig. 1), consisted of a cylindrical piece of 8 mol% YSZ (Vesuvius McDanel), approximately 20 mm length, 6 mm o.d., 4.5 mm i.d., cut with a diamond saw (Leco). Pt electrodes were prepared in a similar manner as the type I design. After the sensor body was prepared, zeolite NaY powder was packed into the inside as to cover the inside electrode. The final sensor was then heated at 500 °C in a tube furnace to achieve thermal equilibrium before testing.

The third design (type III) (Fig. 1 consisted of a YSZ pellet with two Pt electrodes on the same side (planar structure) with one of the Pt electrodes coated by a layer of zeolite. The YSZ pellet and electrodes were prepared

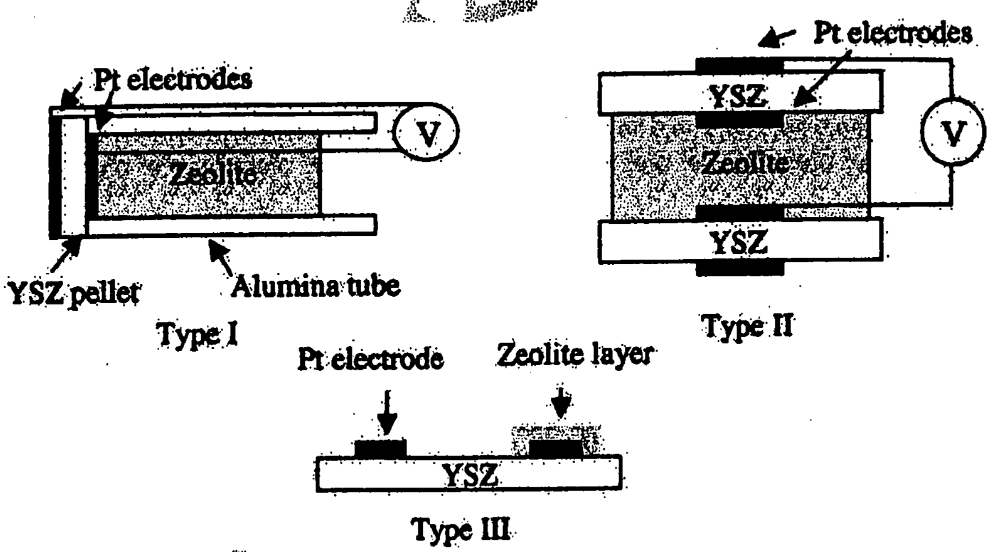


Fig. 1. Schematic representation of the three types of sensors examined.

using the same materials and method as the type I design. A viscous zeolite paste was prepared by mixing zeolite NaY powder with terpineol solvent. The paste was applied with a paint brush over one of the Pt electrodes. After the paste application the sensor was heated in a tube furnace at 500 °C for 2 h to evaporate the terpineol solvent and stabilize the coating.

### 2.2. *Sensing apparatus*

The gas sensing experiments were performed within a quartz tube located inside a high-temperature tube furnace (Lindberg Blue model). The sensor rested on a quartz base while the two sensor wires were connected to two Pt wires threaded onto the quartz tube, which led outside the furnace. The tube furnace was used to heat and cool the sensor at a programmed rate as well as maintaining at a temperature between 500 and 700 °C depending on the experiment. Air, $N_2$ and combustion gases such as NO (2000 ppm source tank), $NO_2$ (1000 ppm source tank), and CO (2000 ppm source tank), were metered through Sierra brand mass flowmeters to form gas mixtures of various compositions, with a volumetric flow rate of 100 $cm^3$/min. The voltage output of the sensor response to changes in the gas concentrations was monitored by a Hewlett-Packard multimeter (34401A) and recorded by Hewlett-Packard Benchlink software on a Windows Pentium based PC.

## 3. Results

The sensor design developed in this study is based on the well-known principles of mixed potential generation upon exposure of a Pt–YSZ interface to NO [8,9]. The two competing reactions at the Pt–YSZ surface upon exposure to $NO/O_2$ are

$$NO + O^{2-} \rightarrow NO_2 + 2e^- \quad (1)$$

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (2)$$

Using these reactions as the basis, we have focused on a sensing strategy outlined below, along with sensor results, interference effects, novel sensor designs and testing of sensors in automotive exhausts.

### 3.1. *Sensing strategy*

Fig. 2A shows a closed-end tube of YSZ, where it is possible to expose the two sides (external and internal parts of the tube) to different gas environments. Fig. 2B and C show the potentials generated between the two electrodes at 500 °C for a fixed $O_2$ (3%) inside the tube, whereas the outside environment is varied from NO (800 ppm) to NO (800 ppm) + $NO_2$ (100 ppm) in a background of 3% $O_2$. Upon introduction of $NO_2$, the signal changes from −21 to −10 mV. This is because in addition to the reactions (1) and (2), another electrochemical reaction:

$$NO_2 + 2e^- \rightarrow NO + O^{2-} \quad (3)$$

also occurs, thus, altering the mixed potential. Thus, if an asymmetry of $NO/NO_2$ is created on two sides of a Pt–YSZ sample, it should lead to a potentiometric signal and is the basis for the sensing strategy developed in this paper.

### 3.2. *Reaction of $NO/O_2$ on zeolites*

Zeolites are microporous aluminosilicates with high internal surface area and porosity. We have examined zeolite Y,

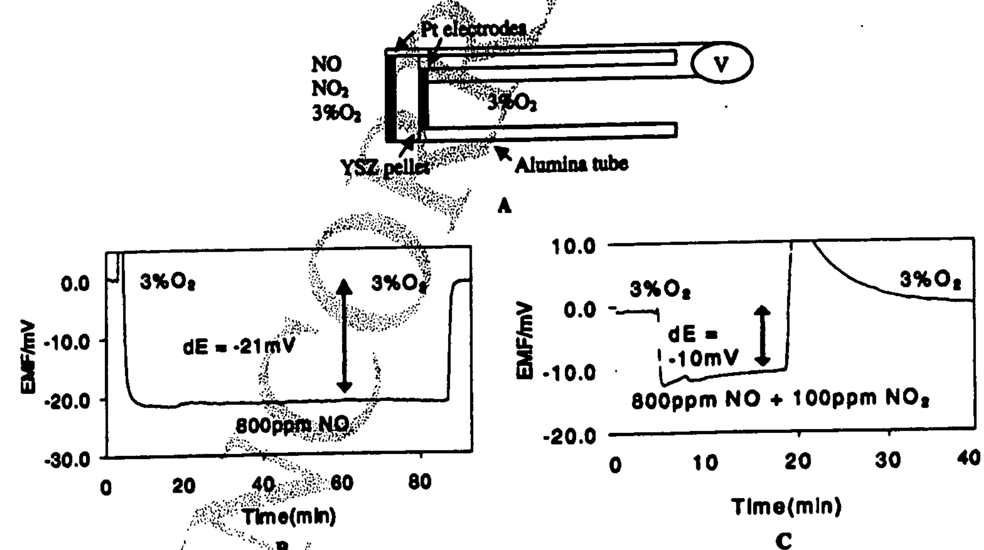


Fig. 2. (A) Design of the sensor with different gas atmospheres on two sides. (B) Sensor response with 800 ppm NO/3% $O_2$ on the outside and 3% $O_2$ inside. (C) Sensor response with 800 ppm NO + 100 ppm $NO_2$ on the outside and 3% $O_2$ inside. All data at 500 °C.

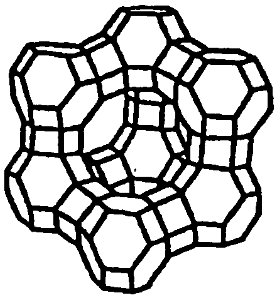

Fig. 3. Schematic representation of a supercage of zeolite Y.

which is made of interconnected supercages of 13 Å sharing 7 Å windows (Fig. 3). For this study, the $Na^+$ exchanged form of the zeolite was used and is labeled, henceforth, as NaY. The reaction of NO on zeolite Y in 3% $O_2$ was analyzed by chemiluminescence techniques. Upon passing 1000 ppm NO through NaY at 500 °C, it was noted that the chemiluminescence signal decreased by $11 \pm 3\%$. There was no evidence of $N_2$ or $N_2O$ formation by gas chromatography, indicating that NO is being oxidized to $NO_2$ upon passing through the zeolite. In the absence of zeolite, under identical conditions of temperature and reactor, the decrease in NO signal was on the order of 1%. Thus, the zeolite provides a medium to alter the $NO/NO_2$ balance and was incorporated into the sensor design.

### 3.3. Sensor design

Fig. 1 shows the three sensor designs that we have investigated. In developing these designs, the strategy is to build asymmetry between the two Pt electrodes by covering one of the electrodes with NaY. Fig. 4A shows the responses of a blank (no NaY coating) and NaY coated planar (type III) sensor for 0–800 ppm NO in 3% $O_2$. It is evident that the presence of NaY causes an enhanced signal towards NO. All three sensor designs showed similar behavior towards NO, as demonstrated in Fig. 4B for a tubular (type I) design. Because of the asymmetry provided by the zeolite layer, it becomes possible to expose the complete sensor to the sensing gases without the need for a reference. Fig. 4C compares the sensitivity plots for the three designs. The voltage follows a linear dependence with the logarithm of the NO concentration. The reproducibility of sensor performance is typified by the insert in Fig. 4C for data obtained from three planar sensors where the signal varia-

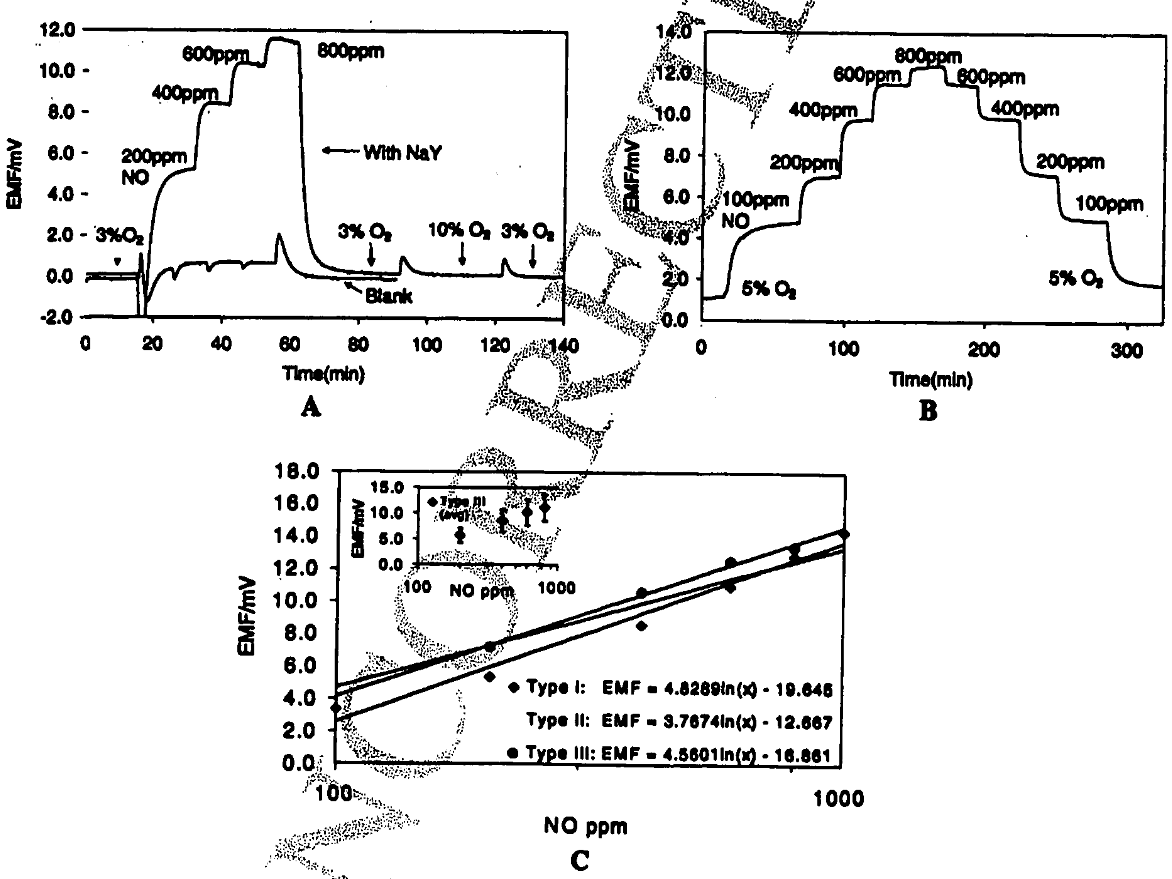


Fig. 4. (A) Sensor response for type III sensor with and without zeolite and exposed to NO between 0 and 800 ppm. (B) Sensor response for type II sensor. (C) Comparison of type I–III sensor responses to NO (insert shows the standard deviation of the data obtained from three different type III sensors). All data at 500 °C.

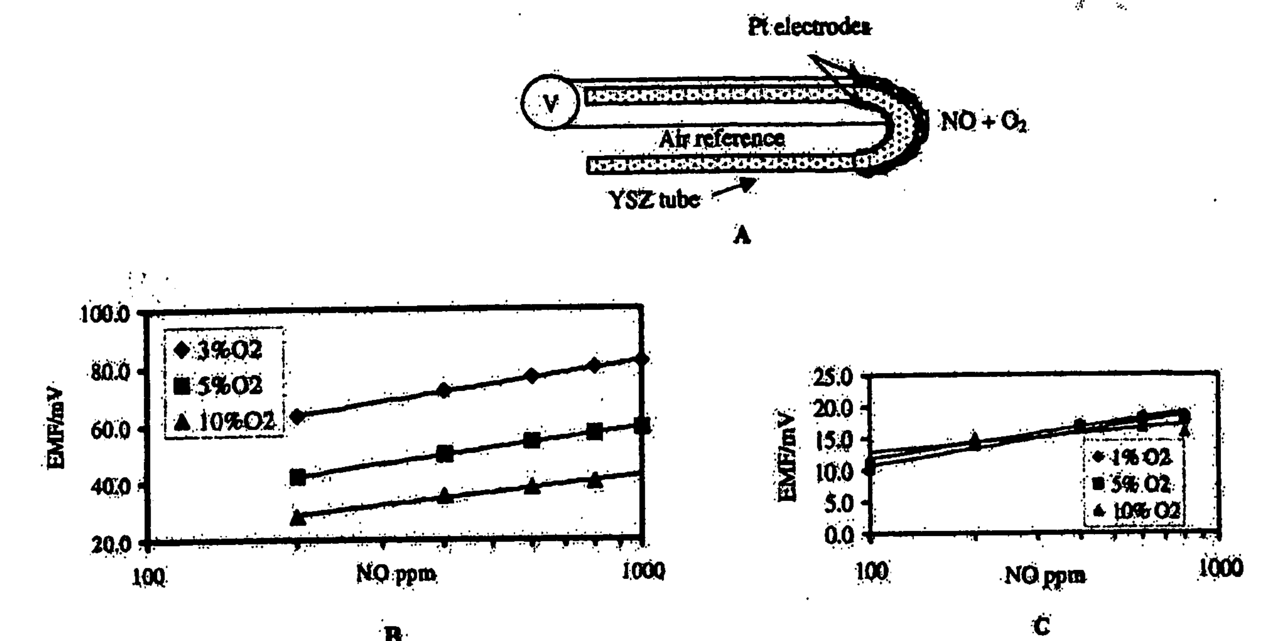


Fig. 5. (A) Air reference sensor diagram. (B) NO calibration curves for varying $O_2$ concentrations on the outside. (C) NO calibration curves for a type II sensor with varying $O_2$ concentrations. All data at 500 °C.

tion for one standard deviation is shown. The variations are likely due to factors in the fabrication process, including the size and thickness of the Pt electrodes, and the zeolite film thickness.

### 3.4. Interference effects

#### 3.4.1. Oxygen

Since YSZ is an oxygen ion conductor, any imbalance of $O_2$ on the two Pt electrodes will alter the baseline. This is demonstrated by using a YSZ closed-end tube type sensor (Fig. 5A) with an air reference where the oxygen inside the tube is at 21%, whereas the outside of the sensor is exposed to NO (100–1000 ppm) at varying oxygen levels similar to a combustion environment. Fig. 5B shows the NO calibration curves for this sensor. If a similar experiment is done with a zeolite-based sensor (e.g. type II in Fig. 1), the calibration curves collapse to approximately the same line (Fig. 5C), demonstrating that the level of $O_2$ at both Pt electrodes is similar, primarily because the microporosity of zeolite allows for $O_2$ transport to the underlying Pt electrode. Another manifestation of the same effect can be seen in Fig. 4A with the planar sensor (type III), where changing $O_2$ levels does not alter the background signal.

#### 3.4.2. Carbon monoxide

Fig. 6A shows the calibration curves obtained with CO using sensor type II and its dependence on the $O_2$ concentration of the background gas. There is a strong signal from CO due to the electrochemical reaction:

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (4)$$

However, the slope of the calibration curve, which is a measure of sensitivity, decreases with increasing $O_2$ concentration. Fig. 6B shows the sensor trace to both CO and NO in 21% $O_2$, where the sensor appears to be almost

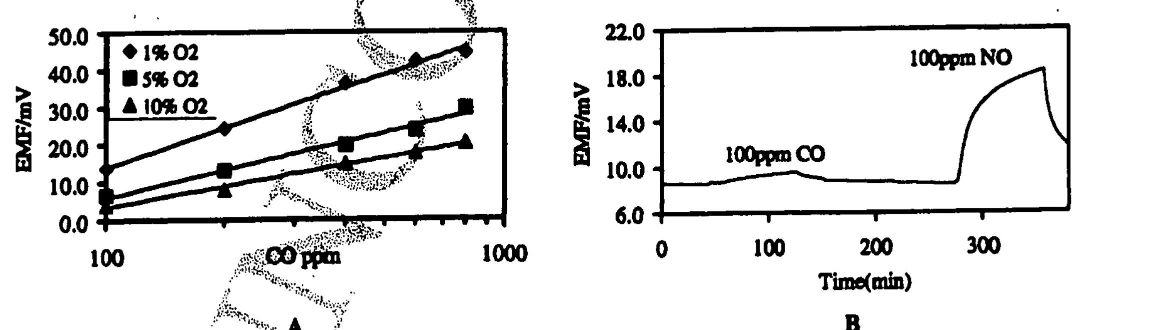


Fig. 6. (A) CO calibration curves obtained with varying $O_2$ concentrations. (B) Comparison of CO and NO sensing responses at 21% $O_2$ and 500 °C.

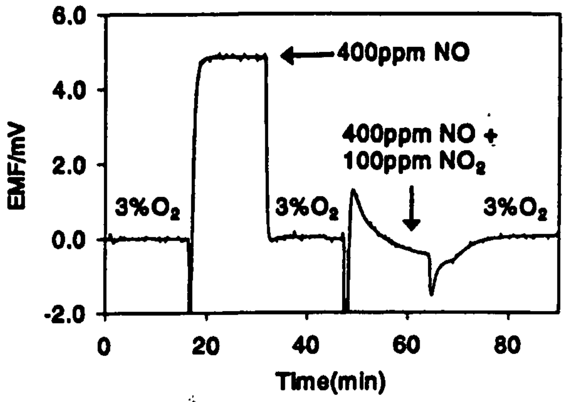


Fig. 7. Demonstration of interference from $NO_2$ for NO sensing on a planar type III design at 500 °C.

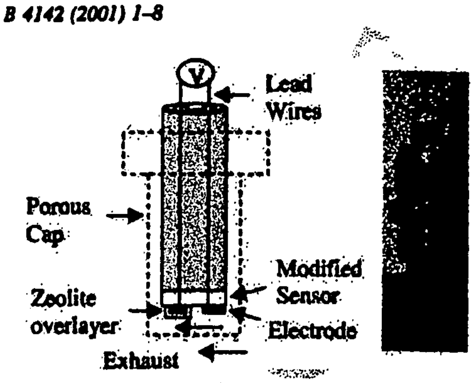


Fig. 8. Schematic of a prototype exhaust sensor assembly and a picture of the probe.

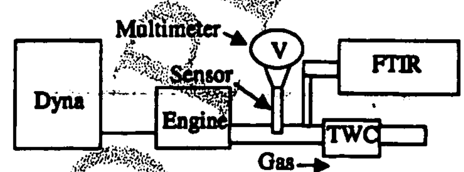


Fig. 9. Layout of automotive exhaust sensing set-up (dyna, dynamometer; engine, V-8 automotive engine; FTIR, Fourier transform IR; TWC, three-way catalyst).

insensitive to CO. Our explanation for the gradual decrease in CO signal with $O_2$ is that the CO gets oxidized on the Pt surface at the higher background $O_2$ levels, before it can reach the Pt–YSZ interface for the electrochemical reaction and the oxidation product $CO_2$ is electrochemically inactive.

### 3.4.3. Nitrogen dioxide

Fig. 7 compares the potentiometric response of a planar sensor (type III) to 400 ppm NO and 400 ppm NO + 100 ppm $NO_2$ in 3% $O_2$ at 500 °C. It is clear that in the presence of $NO_2$, the signal for NO is considerably diminished, indicating significant interference.

### 3.4.4. Temperature effects

Using the sensor type I in Fig. 1, we measured the NO response in a fixed $O_2$ concentration (5%) at temperatures varying from 500 to 700 °C. This temperature range was chosen because YSZ begins to show significant ionic conduction only above 450 °C and zeolite Y retains a crystalline structure up to 750 °C. It was observed that the sensitivity of the sensor decreased with increasing temperature with virtually no sensor response at 700 °C. We propose diminished adsorption of NO at the triple points on the Pt–YSZ interface at higher temperatures. This temperature dependence is consistent with previous measurements, e.g. on $CdCr_2O_4$ electrodes on YSZ, significant loss of NO sensitivity at 600 °C was reported [13].

## 3.5. Harsh environment sensing

The interest in NO sensors arises because of their possible utility in sensing gases in high-temperature combustion processes. Of particular interest to the community is sensing NO emissions from automotive engines. Because of the high-temperatures and the presence of high flow rates and particulates in the exhaust, the sensor needs appropriate packaging. The planar sensor (type III) lends itself to a possible packaging design that can survive the harsh environments. Fig. 8 shows how the planar sensor has been incorporated into a spark plug probe along with a picture of the sensor assembly. To improve the mechanical stability of the zeolite layer in a high flow environment a zeolite pellet was placed on top of the zeolite powder and bonded to the YSZ pellet around the edges with Ceramabond. This sensor was tested in an automotive engine set up shown in Fig. 9. An on-line IR analyzer was used to verify the sensor response. The level of NO in the emission was altered by adjusting the engine speed and a typical NO emission profile

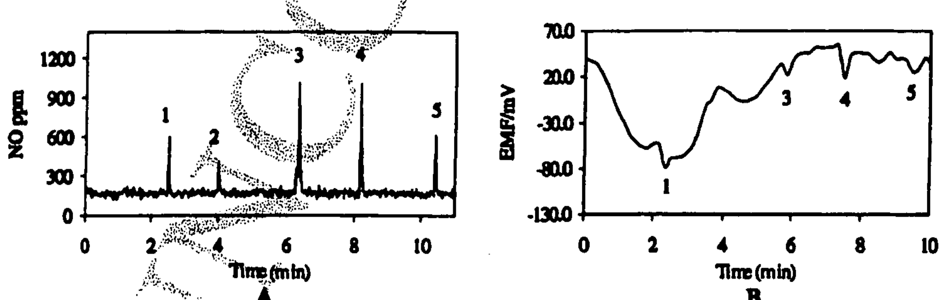


Fig. 10. (A) IR gas analyzer response for NO to five engine throttles. (B) Sensor response for the same five engine throttles.

as measured by the IR is shown in Fig. 10A. The output of the NO sensor is plotted in Fig. 10B and the peaks follow a similar time profile as the IR output (except for event 2, where no response of the NO sensor is observed). These preliminary data are encouraging, in that the sensor packaging survived repeated tests. The response time of the sensor is comparable to that of the IR detector. There is a delay in the response of the IR due to the length of the gas transfer line, which accounts for the small absolute time difference in the sensor and IR signals. The temperature of the exhaust stream fluctuated as the engine speed was altered and could be responsible for the changing backgrounds. Heating of the YSZ to minimize the effect of the temperature fluctuations is currently being investigated.

## 4. Discussion

Potentiometric sensors that exploit the differences in mixed potential between two electrodes for gas sensing have been extensively studied. Usually, the strategy is to use two different electrodes for providing asymmetry and, hence, a measurable EMF response upon NO introduction [9,10]. The strategy that we have proposed here is to use two similar Pt electrodes, but provide asymmetry via a chemical reaction that alters the species interacting with the two electrodes. Our choice of zeolite to alter the $NO/NO_2$ balance was based on several studies that show zeolites as catalysts for NO oxidation. The role of zeolites as catalysts for selective catalytic reduction of $NO_x$ has been extensively studied [20] and it has been observed that the reduction is enhanced in the presence of $O_2$. Mechanistic studies have shown that zeolites promote the oxidation of NO to $NO_2$, the latter being involved in subsequent decomposition reactions to $N_2$ and $O_2$. Amongst the zeolites that have been examined for NO to $NO_2$ oxidation are NaY, Na-ZSM-5, H-ZSM-5, H-mordenite and Cu-ZSM-5 [20–23]. All zeolites that have been studied at temperatures in excess of 400 °C were found to establish the $NO/NO_2$ equilibrium in an $O_2$ environment.

Chemiluminescence studies indicate that about 10% of the NO is converted to $NO_2$. Equilibrium calculations [11,13] predict that at 500 °C, the ratio of $NO/NO_2$ in 5% and 0.5% $O_2$ are 4.9 and 32, respectively whereas at 3% $O_2$, we observe the ratio to be close to 8 indicating that the zeolite is promoting the $NO/NO_2$ reaction towards equilibrium. Thus, with the zeolite coating, there is an asymmetry of $NO/NO_2$ profiles at the two Pt electrodes. This asymmetry leads to sensing of NO. However, this also leads to the observation that if $NO_2$ is present in the sensing stream and its concentration changes, then the NO signal is altered. Thus, the present sensor system cannot be used for sensing NO in gas streams where $NO_2$ concentration is also changing. Miura at al. have shown that by using a three-electrode system with chromates as the sensing electrode, selectivity towards NO or $NO_2$ could be accomplished by applying a bias voltage to the sensing electrode relative to a Pt counter electrode, while measuring the voltage relative to a Pt-reference electrode [13,24].

An advantage of the zeolite-based design is the fact that NO response is relatively insensitive to changing $O_2$ profiles in the gas stream, over the $O_2$ concentrations examined in this study (1–10%). This arises from the porous nature of the zeolite, which allows for the penetration of $O_2$ to the Pt–YSZ interface. A part of the oxygen reacts with NO to form $NO_2$, but considering the significant excess of $O_2$ over NO, the $O_2$ concentration change is very small. Another strategy for detecting NO in changing $O_2$ levels is based on multielectrode amperometric sensors, in which diffusion-limited passage of gases to multiple electrodes held at different potentials ensures that oxygen gets completely reduced at the first electrode, followed by NO reduction at the second electrode [25].

Interference from CO can be significant, but under the lean conditions that result in NO formation, the levels of CO should be small. Also, the fact that at high $O_2$ backgrounds, the effect of the CO interference is minimized due to oxidation to $CO_2$ provides possible pathways for minimizing the CO interference.

The strategy of using a catalyst to suppress interference is well recognized in the sensor literature. Ono et al. used a $Na^+$ conductor (NASICON) as the electrolyte and a $WO_3$ and $Pt/SiO_2$ catalyst layer to detect NO and $NO_2$ at 150 °C [26]. Zeolite filters have been used to minimize cross species interferences by chemically reacting the gas to undetectable species [17]. Our strategy is somewhat different, since we are using the zeolite to promote the sensing characteristics. The zeolite-based sensor can also be fabricated with several designs, including a convenient planar design that was incorporated into a spark plug type assembly for measuring NO in automotive exhausts.

From a sensitivity standpoint, the zeolite-based sensor is not as good as the best mixed potential sensors made by using two different electrode materials. Miura et al. found that for a three electrode YSZ plate sensor, where a $CdCr_2O_4$ sensing electrode was polarized at 100 mV with respect to a Pt counter electrode, the sensing electrode signal verses a Pt-reference electrode gave a voltage change of around 30 mV for 200 ppm NO in air [13], whereas for a similar planar design (but without the applied voltage), the zeolite sensor produces a response of approximately 7 mV. The response/recovery times of the present zeolite-based sensor for laboratory tests is of the order of 10 s, while it appears faster in the automotive exhaust tests, presumably because of much higher gas flows.

## 5. Conclusions

By using a microporous aluminosilicate zeolite that promotes the $NO/NO_2$ equilibrium at temperatures of 500 °C and higher, an asymmetry was generated between two Pt

electrodes on YSZ. This asymmetry led to a mixed potential signal, which was proportional to NO concentration (0–1000 ppm) with a logarithmic dependence. The sensor response was stable in varying $O_2$ concentrations, but showed interference from CO and $NO_2$. The range of temperatures over which signals could be measured was 500–600 °C with better sensitivity at the lower temperatures. Several sensor designs were tested, including a planar sensor that was packaged into a spark plug type fitting and tested in an automotive exhaust assembly. The sensor response followed the NO concentration, with comparable response times as the IR detector.

## Acknowledgements

We acknowledge the help from Professor Umit Ozkan for the chemiluminescence experiments. This research was funded by NSF grant EEC-9523358 and EMTEC (which is funded by the Ohio Department of Development).

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